A Point-Contact Study of the Superconducting Gaps in Al-Substituted and C-Substituted MgB_2 Single Crystals

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We present the results of directional point-contact spectroscopy in state-of-the-art $Mg_{1-x}Al_xB_2$ and $Mg(B_{1-y}C_y)_2$ single crystals produced at ETH, Zurich. Fitting the conductance curves of our point contacts, that always feature Andreev reflection structures, we obtained the doping dependence of the gap amplitudes. The results are discussed in comparison with other experimental findings and relevant theoretical predictions. We conclude that the physics of Al-substituted crystals at $x \gtrsim 0.09$ might be governed by phase segregation, while C-substituted crystals unexpectedly show a doping-induced transition to single-gap superconductivity at $y = 0.132$.

Magnesium diboride, MgB_2, represents a unique and lucky combination of different physical properties that make it the highest-T_c intermetallic compound, the only superconducting diboride and the clearest example of two-band superconductor ever discovered. As a matter of fact, most of its physics has been explained rather well within the two-band model in either the BCS [1] or the Eliashberg [2, 3] formulation . Much effort has been made in order to understand whether the peculiar properties of MgB_2 can be in some way tuned and controlled, both in view of applications (where, for example, higher critical fields or smaller anisotropy are required) or for fundamental reasons (to test the predictions of the two-band models concerning the effects of variations in some of the physical quantities that describe MgB_2). In other words, most of the present research work is devoted to investigate the "neighborhood" of MgB_2, that is all the systems that can be obtained from MgB_2 by means of pressure, irradiation, lattice stress, disorder and, over all, chemical substitutions.

Obtaining partial substitution of Mg or B atoms in MgB_2 is a difficult task. Even in the (few) cases of success, e.g. with aluminum and carbon, there are problems of solubility [4], phase segregation [5, 6], inhomogeneities[7] and structural transitions [8]. Most of the substituted samples presently available are polycrystalline, of quality good enough to allow various kinds of experimental investigations that have led to highlight many structural, electronic and superconducting properties of these compounds. However, only a few determinations of the doping dependence of the energy gaps have appeared in literature, both for $Mg_{1-x}Al_xB_2$ [9, 10] and $Mg(B_{1-y}C_y)_2$ [11, 12, 13], and none in single crystals.

In the following, we will present the results of the first systematic study of the energy gaps in $Mg_{1-x}Al_xB_2$ and $Mg(B_{1-y}C_y)_2$ single crystals as a function of Al and C contents, by means of *directional* point-contact spectroscopy (DPCS). We will show that the doping dependence of the gaps is completely different in Al-substituted and C-substituted samples. In $Mg_{1-x}Al_xB_2$ crystals there is no evidence of gap merging and the small gap strongly decreases on increasing x, to become as small as 0.4 meV at $x = 0.21$, while the large gap saturates at about 4 meV at high Al contents. In $Mg(B_{1-y}C_y)_2$ crystals, instead, the π-band gap remains practically unchanged (at most, it shows a small increase), while the σ-band gap decreases and, at $x = 0.132$, the two gaps merge into one of amplitude $\Delta \simeq 3$ meV. The results will be discussed in comparison with other experimental findings as well as with theoretical predictions.

Both the $Mg_{1-x}Al_xB_2$ and the $Mg(B_{1-y}C_y)_2$ single crystals were grown at the Solid State Laboratory, ETH-Zurich (Switzerland) by using a high-pressure technique in a cubic-anvil press, in the same way as the unsubstituted crystals [14]). The partial substitution of Al in

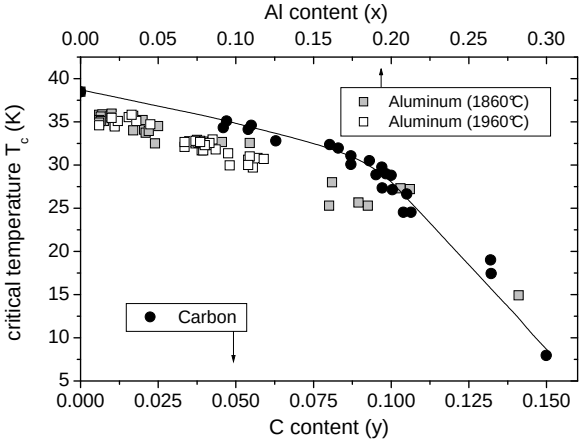

FIG. 1: Experimental dependence of the critical temperature (evaluated from DC magnetization) on the content of Aluminum (top axis) or Carbon (bottom axis) in $Mg_{1-x}Al_xB_2$ and $Mg(B_{1-y}C_y)_2$, respectively. The two sets of points for $Mg_{1-x}Al_xB_2$ refer to different growth temperatures.

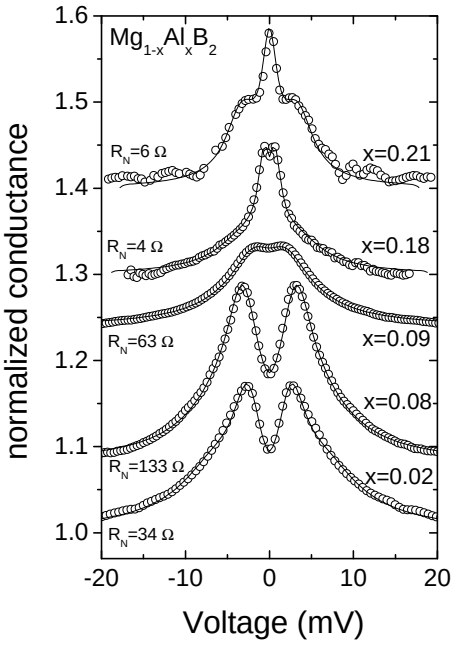

FIG. 2: Symbols: experimental normalized conductance curves of $Ag/Mg_{1-x}Al_xB_2$ point contacts for different Al contents x. The curves are vertically shifted for clarity, and were all measured at 4.2 K apart from the last two ($x = 0.18$, 021) that were measured at 1.8 K. The normal-state junction resistance is also indicated. Lines: best-fit curves obtained with the two-band BTK model (see text for details).

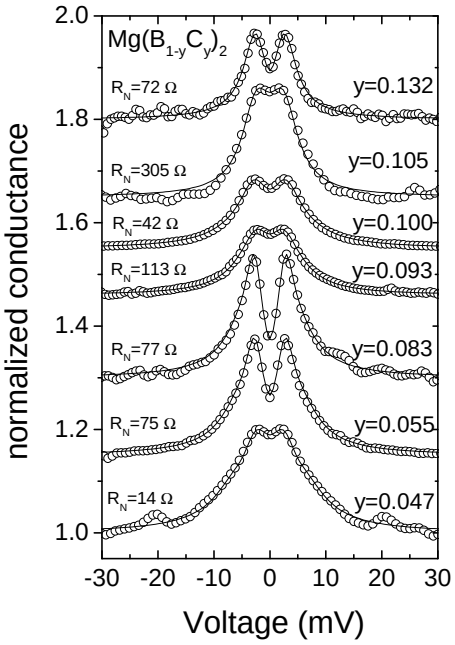

FIG. 3: Symbols: experimental normalized conductance curves of $Ag/Mg(B_{1-y}C_y)_2$ point contacts for different C contents y. The curves are vertically shifted for clarity, and were all measured at 4.2 K. The normal-state resistances are also indicated. Lines: best-fit curves obtained with the two-band or one-band BTK model.

MgB_2 was obtained by replacing part of the Mg precursor with Al [6]. As evidenced by HRTEM, at high doping levels there is a strong tendency to the precipitation of a second phase, in the form of Al-rich layers (probably $MgAlB_4$) perpendicular to the c axis, while no defects are shown in the ab plane. The $Mg(B_{1-y}C_y)_2$ crystals were grown at 1900-1950°C by starting from magnesium, amorphous boron and graphite powder or SiC as a carbon source. In the latter case, no trace of Si was found in the final material [7].

The crystals used for our DPCS measurements had Al contents x (measured with EDX) ranging from 0.02 up to 0.21, and C contents y (evaluated from the cell parameter a) between 0.055 and 0.132. Figure 1 reports the doping dependence of the critical temperature T_c, given by DC magnetization measurements, for both $Mg_{1-x}Al_xB_2$ and $Mg(B_{1-y}C_y)_2$ crystals. Very surprisingly, the two curves turn out to be rather similar if plotted versus the atomic content of Al and C (x and $2y$, respectively).

Directional point-contact measurements were performed by using the pressure-less ("soft") technique described elsewhere [15, 16] that consists in using a small ($\varnothing \leq 50$ μm) drop of Ag conductive paint as the counter-electrode, instead of the usual metallic tip pressed against the sample surface. This ensures greater contact stability on thermal cycling and allows making the contacts on the side of the (very thin) crystals, so as to inject the current mainly parallel to the ab planes. In unsubstituted MgB_2, this is the best configuration for a contemporaneous measurement of *both* the gaps [2, 15]. The experimental conductance curves (dI/dV vs. V) of our point contacts were normalized to the normal-state conductance to allow comparison with the Blonder-Tinkham-Klapwijk (BTK) model for superconductor/normal metal interfaces [17]. All our contacts were in the ballistic limit and had small potential barrier. Indeed, the conductance curves show clear Andreev-reflection features. In particular, they present clear maxima at energies roughly equal to the small gap, Δ_π, but (in spite of the current injection along the ab plane [15]) only smooth shoulders at energies corresponding to the large gap, Δ_σ.

Figure 2 reports some normalized experimental conductance curves (symbols) measured in single crystals with different Al contents. All the curves were recorded at 4.2 K apart from the last two ($x = 0.18, 0.21$) that were measured at 1.8 K because the thermal smearing at 4.2 K was already comparable to the energy width of the Andreev-reflection structures. Even at a first glance, two distinct doping regimes can be identified. For $x < 0.09$, the conductance peaks corresponding to Δ_π slightly move outwards with respect to the undoped case. For $x > 0.09$, instead, the peaks shrink very fast on increasing x and finally merge in a single sharp maximum at zero bias, indicating a fast decrease in Δ_π. The clear narrowing of the whole conductance curves in passing from the low-x

to the high-x regime indicates that also Δ_σ undergoes a significant (and sudden) change around $x = 0.09$.

A quantitative evaluation of the gap amplitudes can be given by fitting the conductance curves with the BTK model generalized to the two-band case, that has been shown to work well in pure MgB_2 [15, 18]. The best-fitting curves, that agree well with the experimental data, are shown as solid lines in Fig.2. The fitting function contains 7 parameters: the gaps Δ_σ and Δ_π, the barrier parameters Z_σ and Z_π, the lifetime broadening parameters Γ_σ and Γ_π, plus the weight of the π band in the total conductance, w_π. Hence, one could object that the fitting procedure should give rather large uncertainties on the gap values. Actually: i) the value of Δ_π is quite well determined by the energy position of the conductance peaks, and thus its uncertainty is necessarily small; ii) the values of both Δ_π and Δ_σ were confirmed, up to $x = 0.09$, by the independent, three-parameter fit of the σ and π-band contributions to the conductance, whose separation was possible by applying a suitable magnetic field to the junction, as explained elsewhere [15, 18]. This was not possible for x>0.09, where even weak fields depress the σ-band gap and leave Δ_π almost unchanged.

Fig.3 reports a subset of the conductance curves measured at 4.2 K in various $Mg(B_{1-y}C_y)_2$ single crystals with different y. In this case there are no dramatic changes in the amplitude of the small gap Δ_π, while the constant narrowing of the Andreev-reflection features indicates a decrease in the σ-band gap. As in Fig.2, solid lines represent the two-band BTK best-fitting curves. In various cases, we were able to separate (and fit separately) the partial σ and π-band conductances by applying a suitable magnetic field, thus achieving a higher-precision determination of the gap amplitudes. (Actually, the effect of the field on the conductance curves of the $Ag/Mg(B_{1-y}C_y)_2$ point contacts is rather complex and will be the subject of a forthcoming paper).

The gap values extracted from the fit of the conductance curves are reported in Fig.4 for $Mg_{1-x}Al_xB_2$ (upper panel) and $Mg(B_{1-y}C_y)_2$ (lower panel). The trends are roughly indicated by dashed curves that are simply guides to the eye. The x dependence of the gaps in $Mg_{1-x}Al_xB_2$ clearly reflects the aforementioned distinction between two regimes, delimited by the "threshold" value $x = 0.09$. In the low-x regime, the behaviour of Δ_σ and Δ_π is compatible with an increase in *inter-band* scattering [1]. Within the two-band model in the Eliashberg formalism, the gaps measured in the $x = 0.08$ sample ($\Delta_\pi = 3.1$ meV, $\Delta_\sigma = 6.1$ meV) can indeed be obtained from those of MgB_2 by only increasing the interband scattering up to $\Gamma_{\sigma\pi} \simeq 1.55$ meV. If one also takes into account all the other effects of Al substitutions (i.e. the changes in the DOS due to electron doping [19] and the stiffening of the E_{2g} phonon mode [20]), the experimental trend of the gaps in the low-x regime is qualitatively reproduced [21]. Things change completely

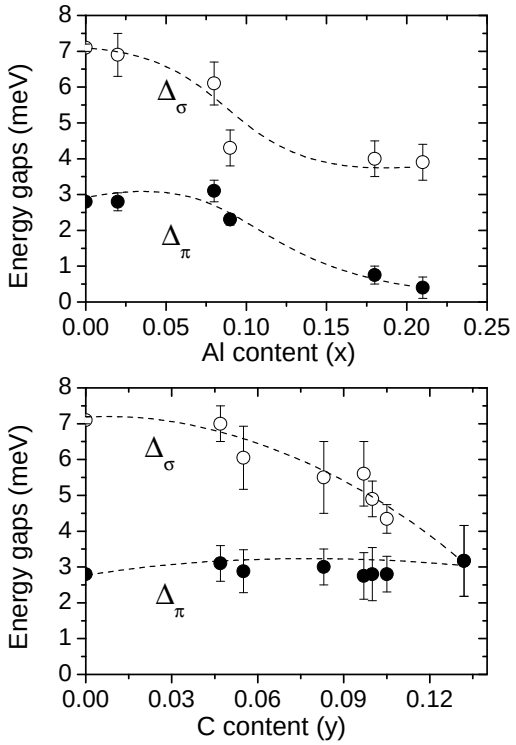

FIG. 4: Upper panel: dependence of the energy gaps, Δ_σ and Δ_π, on the Al content x in $Mg_{1-x}Al_xB_2$. The lines are only guides to the eye. Lower panel: dependence of the gaps on the C content y in $Mg(B_{1-y}C_y)_2$. Lines are only guides to the eye.

above $x = 0.09$, where the experimental data contrast with all present theoretical models. For high doping levels a merging of two gaps into one is predicted either by simply increasing the interband scattering [1] or by including all the effects of Al substitution in the Eliashberg theory [21]. In the first case, a BCS gap $\Delta \approx 4.1$ meV and a critical temperature $T_c \approx 26$ K are expected in the so-called "dirty", isotropic limit [1]; in the second case, the gap merging is predicted to occur around $x = 0.33$, when $\Delta_\sigma = \Delta_\pi \approx 3$ meV and $T_c \simeq 20$ K [21]. However, the experimental results show no evidence of gap merging: Δ_π decreases down to 0.4 meV at $x = 0.21$ (with $T_c = 20$ K) while Δ_σ seems to saturate at about 4 meV. The failure of the simple "interband scattering" picture is not really surprising, since electron doping and phonon stiffening cannot be neglected [20]. The failure of the more complete Eliashberg two-band model is much more interesting. One possible explanation is that phase segregation (indeed occurring in our crystals at $x \gtrsim 0.10$) plays a major role in our result, causing an unpredicted transition to a substantially different physical system. However, it is worth saying that also recent gap measurements in segregation-free $Mg_{1-x}Al_xB_2$ polycrystals by means of PCS [10] have given no evidence of gap merging up to $x = 0.3$, when T_c is as low as 24 K. Instead, the values $\Delta_\sigma = 2.0$ meV and $\Delta_\pi = 0.5$ meV have been found,

that agree rather well with those given by specific-heat measurements in the same samples but contrast with the predictions of all present theories [1, 21, 22].

The dependence of the gaps in $Mg(B_{1-y}C_y)_2$ on the carbon content y, reported in the lower panel of Fig.4, is much more regular. While Δ_π slightly increases, Δ_σ decreases monotonically until, at $x = 0.132$, *only one gap* of amplitude $\Delta = 3.2 \pm 0.9$ meV is observed [26]. Each point is the average of different gap values measured in different contacts, whose spread is indicated by the error bar. The large uncertainty at $x = 0.132$ may arise from carbon-content inhomogeneity on a length scale of the order of ξ [7], that unfortunately can be detected by PCS. The overall gap trend does not differ much from that predicted by the two-band Eliashberg model for Al substitutions. Despite the different lattice sites occupied by Al and C, some effects of the C substitution are indeed very similar to those of Al doping: the decrease in T_c (see fig.1), the filling of the σ bands due to electron doping [23], the stiffening of the E_{2g} phonon mode and the consequent decrease in the electron-phonon coupling [24]. It is thus possible that, with suitable input from experimental data, the two-band model can reproduce the results presented here. As far as the "interband scattering" picture is concerned, let us just remind that, in principle, carbon substitutions should not increase the interband scattering [25]. On the other hand, critical field measurements in C-doped single crystals have evidenced a reduction in the superconducting anisotropy [24]. The extrapolation of this result above $y = 0.10$ would lead to almost isotropic superconducting properties accompanied by *anisotropic* bandstructure, as would be expected for strong interband scattering.

As we did in the case of $Mg_{1-x}Al_xB_2$, it is worth comparing our results with other gap measurements in $Mg(B_{1-y}C_y)_2$ reported in literature. Early μ^+SR studies of $Mg(B_{1-y}C_y)_2$ polycrystals in the extreme low-doping region ($y \leq 0.03$) [13] showed a fast linear decrease of the gaps on increasing y (with the same slope for Δ_σ and Δ_π), in such a way that, at $y = 0.03$, $\Delta_\sigma = 4.8$ meV and $\Delta_\pi = 1.3$ meV. These values are much smaller than ours, and also disagree with those determined, in polycrystalline samples, by PCS [11] and tunneling [12]. In these last papers, the retention of two-gap superconductivity was observed (as in our case) up to $y = 0.1$, where $T_c = 22$ K. In the recent paper by Holanová *et al.*, a linear decrease of the gaps vs T_c (with different slopes for Δ_σ and Δ_π) was claimed. The trend they evidenced for Δ_σ is in very good agreement with ours, despite a systematic difference in the absolute values (that are all smaller than ours by 0.8 meV). On the contrary, the linear decrease in Δ_π contrasts with our findings. These disagreements might be due to the different nature and quality of the samples, but further investigations are required to clarify this important point.

In conclusion, we have presented the results of the first systematic investigation of $Mg_{1-x}Al_xB_2$ and $Mg(B_{1-y}C_y)_2$ single crystals by directional point-contact spectroscopy. We have shown that the dependence of the gaps on the Al content contrasts will all present theories and is probably affected by phase segregation above $x \simeq 0.10$. In C-substituted crystals, instead, we have found the first evidence of gap merging, predicted theoretically as a result of the doping-induced changes in the DOS and in the phonon frequency and/or by the increase of interband scattering. This finding might provide the longed for, final test of the theoretical models for two-band superconductivity.

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